

Nitrogenated organic aerosols as cloud condensation nuclei

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[1] One important role of anthropogenic aerosol particles is their influence on climate by acting as cloud condensation nuclei. However, these particles are diverse in composition and mixing state, and our knowledge of which particle types act as cloud condensation nuclei is incomplete. Here we present direct measurements of individual organic particles that nucleated cloud droplets in the atmosphere. These results indicate that nitrogenated organic aerosol particles can act as cloud condensation nuclei without being mixed with inorganic material, and thus influence climate through cloud formation. **Citation:** Twohy, C. H., J. R. Anderson, and P. A. Crozier (2005), Nitrogenated organic aerosols as cloud condensation nuclei, *Geophys. Res. Lett.*, 32, L19805, doi:10.1029/2005GL023605.

1. Introduction

[2] The largest uncertainty in predicting human impact on climate is related to the effects of anthropogenic aerosol particles, in particular their effects on clouds. Anthropogenic particles may act as cloud condensation nuclei (CCN). Increased numbers of CCN can increase the number of cloud droplets and decrease cloud droplet size [Twomey, 1974]. The net effect is to theoretically make clouds more reflective to solar radiation, although this assumes a constant liquid water path that does not always occur [Brenquier *et al.*, 2003; Twohy *et al.*, 2005]. Clouds with smaller drops are less likely to precipitate and thus may have longer lifetimes, which could further enhance the cooling effect of increased CCN [Albrecht, 1989].

[3] The large variety of aerosol particles in the atmosphere and our incomplete knowledge of their CCN behaviour contributes to the uncertainty in determining their climatic effects. In order for a particular aerosol particle to actually grow into a cloud drop (“activate”), the water content in its environment must exceed a critical supersaturation (S_c). Simple theory indicates that S_c is anticorrelated with the number of soluble ions in the particle and, hence, is dependent on particle composition and size. Changes in critical supersaturation and droplet growth characteristics may be introduced by partly soluble substances, soluble gases, and surface tension effects [Shulman *et al.*, 1996; Hitzenberger *et al.*, 2002; Charlson *et al.*, 2001].

[4] Natural soluble particles such as sea-salt as well as pollutants like sulfate and nitrate can act as CCN. Large quantities of carbonaceous aerosols are emitted by industrial activity, and their mass concentrations may sometimes be as

great as those of other inorganic particle species [Hobbs, 1999]. Carbonaceous aerosols are composed of both light-absorbing “black carbon” and more complex organic carbon. Bulk cloudwater measurements indicate that organic constituents are common in clouds and can represent a significant portion of total solute mass [Herckes *et al.*, 2002a, 2002b; Facchini *et al.*, 1999]. In a marine environment, organic compounds were found to be correlated with CCN number [Novakov and Penner, 1993]. Scant evidence exists, however, to judge whether organic species act as CCN on their own in the atmosphere or whether they are internally mixed with soluble inorganic species that impart the CCN activity. While laboratory studies [Novakov and Corrigan, 1996; Raymond and Pandis, 2002] and at least one field experiment [Noone *et al.*, 2000] have suggested that organics alone can act as CCN, another study indicated that organics in droplet residual particles were always mixed with inorganic species like sulfates [Gieray *et al.*, 1997]. Studies too numerous to detail here indicate that mixtures of organic and inorganic species exhibit complex cloud-nucleating effects [e.g., Russell *et al.*, 2000; Bilde and Svenningsson, 2004; Lohmann *et al.*, 2004]. High molecular-weight organic compounds have been found in polluted cloudwater [Fuzzi *et al.*, 2002; Herckes *et al.*, 2002a, 2002b], and even those with low solubility can act as CCN if they have a small contact angle with water and provide a site for water to condense [Raymond and Pandis, 2002].

[5] Here we present field measurements of individual organic particles that nucleated cloud droplets in a polluted region. These results show not only that organic aerosols can be mixed with inorganic species such as sulfates in clouds, but also that organics can act as CCN on their own merit.

2. Experiment and Results

[6] The Indian subcontinent is one of the most polluted regions in the world, with carbonaceous material contributing about half of the fine particle mass at low altitudes [Mayol-Bracero *et al.*, 2002]. As part of the Indian Ocean Experiment [Crutzen and Ramanathan, 2001], small cumulus clouds over the Indian Ocean were sampled from a C-130 research aircraft. This region was chosen for its proximity to both highly polluted air downwind of commingled plumes from India as well as to clean Southern Hemisphere air south of the Intertropical Convergence Zone (ITCZ). A counterflow virtual impactor [Noone *et al.*, 1988] was used to separate droplets in these clouds from interstitial aerosol particles and gases. Droplets were impacted directly into a nitrogen stream heated to 50°C to evaporate them. Individual non-volatile residual particles were then collected and measured by various techniques [Twohy *et al.*, 2001].

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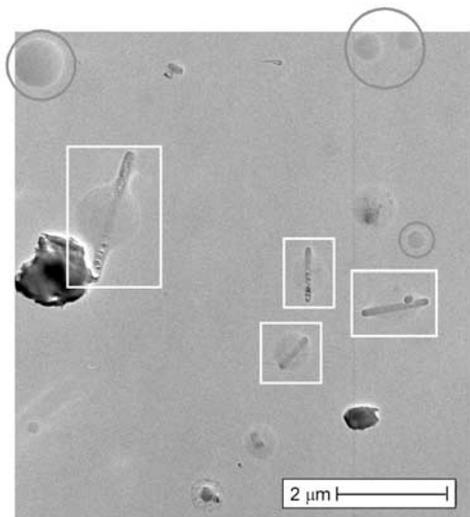


Figure 1. Transmission electron microscope image of cloud residual particles collected in polluted air downwind of India. Particles in orange or white boxes are S-containing crystals embedded in an organic matrix, while those in blue or grey circles are solely organic. See color version of this figure in the HTML.

[7] About 800 km downwind of the Indian coastline on 27 February 1999, residual particles from cloud droplets were collected on substrates for both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). This polluted case was chosen since a majority (73%) of the total droplet distribution was large enough to be sampled efficiently by the CVI. These droplets clearly formed on particles with favorable CCN activity, as the median critical supersaturation of the residual droplet nuclei was measured to be only 0.04%, in contrast to 0.22% for the ambient aerosol [Twohy *et al.*, 2001]. Automated SEM [Anderson *et al.*, 1996] and Energy Dispersive X-ray Spectrometry were used to detect and cluster the elements present in 900 individual residual particles. Only particles larger than about 0.1 μm diameter were analyzed, and only elements with atomic numbers greater than 8 were reliably detected—thus carbon, nitrogen, and oxygen were not identified by this initial analysis technique. Twenty-three percent of the particles contained no detectable elements, indicating they contained primarily carbon and/or nitrogen and oxygen. The only detectable element in 22% of the residual particles was sulfur; these particles were presumably sulfates or internally mixed sulfates and carbonaceous material. Seventeen percent of the particles were sea-salt derived, mostly reacted to sodium sulfate and sodium nitrate. (The remaining 38% of the particles contained various elements including potassium, silicon, sodium, calcium, and metals, and internal mixtures of these types with sulfur).

[8] Figure 1 shows a TEM micrograph of the collected residual particles. Several different morphologies are visible, revealing the non-uniformity of aerosol particles that act as CCN under polluted conditions. Particles with relatively homogeneous structure are circled. These particles were not observed in clean cloud samples collected south of the ITCZ under identical conditions, so they are not sampling artifacts. Their morphology is not characteristic

of ammonium sulfate, sea-salt, black carbon, or soil-dust [Li *et al.*, 2003]. These morphologically homogeneous particles were analyzed with high spatial resolution elemental analysis, utilizing Electron Energy Loss Spectrometry (EELS) and scanning TEM. A nanometer size focused electron beam was scanned rapidly in a line across the center of the particle, starting and ending on the polycarbonate film outside the particle so that the background signal could be subtracted. The scan was performed rapidly with a dwell time per pixel of 1s or less to minimize the influence of electron radiation damage on the analysis. A typical annular dark-field image and electron energy-loss spectrum from one of these aerosol particles are shown in Figures 2a and 2b, respectively. In these particle types, the energy-loss spectra always show the presence of a large carbon peak and varying amounts of N, S and O (note that H is not detectable with EELS). Figure 2c shows the derived elemental profiles. Relative atomic concentration ratios of these elements were determined using standard processing routines [Egerton, 1978; Crozier *et al.*, 2004] for many particles from this sample with the same morphology. The approximate atomic percentages derived from the analysis were carbon 70% and nitrogen 20%, with the balance being sulfur and oxygen. Some mass loss may still have taken place during the analysis but we expect this to be a small effect, since the rapid scan technique minimizes the electron dose at any one point during data acquisition. The EELS analysis thus proves that these particles and others with similar morphology were organic, with nitrogen being the second most abundant element.

[9] Once the morphology of the organic particles was established, multiple low-dose high-resolution images of the impacted samples were visually examined to estimate the fraction of organic particles in both the in-cloud CVI sample and in a sample collected in clear-air below cloud immediately afterward. The low-dose technique that we used [e.g., Pan and Crozier, 1993] prevented ammonium sulfate par-

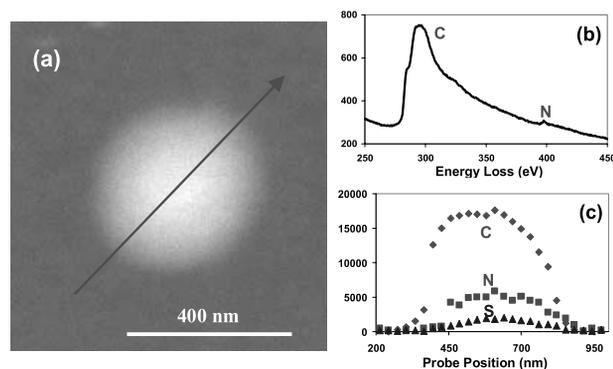


Figure 2. Detailed analysis of organic droplet residual particle. a) Annular dark-field electron micrograph from 400 nm organic particle. Diagonal arrow shows path followed by electron probe during acquisition of spatially resolved EELS spectra. b) Typical energy-loss spectra recorded from organic particle showing C and N signal (intensity in arbitrary units). c) Elemental profiles obtained from linescan across particle showing distribution of C, N and S in relative units. The signal strengths have been scaled so that the signal ratio equals concentration ratio. See color version of this figure in the HTML.

Table 1. Comparison of Below-Cloud and Droplet Nuclei Organic Concentrations

Sample	Total N, cm ⁻³ ^a	N > 0.1 μm, cm ⁻³ ^b	N Organic > 0.1 μm, cm ⁻³	Actual # > 0.1 μm Analyzed Visually
Below-cloud	2002	814	41	400
Droplet nuclei	122	69	21	193
Fraction activated	0.06	0.08	0.51	-

^aConcentration > 0.01 μm diameter measured by condensation particle counter.

^bConcentration > 0.1 μm diameter measured by optical particle counter.

ticles from “bubbling” thus ensuring that they were not destroyed during imaging recording. Table 1 shows the number concentration of particles in different size ranges measured in the ambient below-cloud air and sampled as droplet nuclei. The number concentration of organics in each sample was estimated using the percentage of organic particles counted on the grid and the total number concentration of particles larger than 0.1 μm measured in-situ by an optical particle counter. Table 1 shows that while less than 10% of all particle types >0.1 μm were incorporated into cloud droplets, about 50% of the organic particles were activated. This indicates not only that these organics act as CCN in this polluted region, but that they are more efficient at participating in cloud formation than the general population of particle types. A simple calculation shows that an increase in droplet number of 1/3 to 1/2 due to organic CCN would correspond to a substantial albedo increase of 0.02 to 0.06 for an initial cloud albedo of 0.50 [Platnick and Twomey, 1994]. This assumes a constant liquid water path.

[10] Some of the larger residual particles (circled in orange in Figure 1) show a rod-shaped crystalline phase embedded in an apparently liquid matrix. Both phases of this particle type were analyzed with EELS. The liquid phase exhibited an organic composition similar to the particles circled in blue, while the crystalline phase was sulfur-rich and was most likely ammonium sulfate (possibly originally present as bisulfate). The epitaxial relationship of the organic droplet to the ammonium sulfate crystal suggests that surface energy considerations favor growth on the ends of the sulfate crystal not enclosed within the organic droplet, resulting in the elongate prismatic habit observed. These mixed particles would have been identified only as sulfates by the automated SEM technique. Thus, the relative importance of organics may have been underestimated by that method. Particles with this mixed-phase morphology were also sampled off the coast of Southern California in another experiment.

[11] Organic nitrogen has been found in rainwater over much of the globe [Cornell *et al.*, 2001]. Sources include combustion, agriculture, and biomass burning, all of which could be important in the Indian subcontinent. Organic nitrogen compounds were present in a significant fraction of sub-micron aerosol particles detected in the INDOEX sampling region (K. Prather, personal communication, 2004). Dissolved organic nitrogen has been measured in bulk California fogwater at comparable concentrations as those measured in the nearby ambient aerosol, and with similar carbon to nitrogen ratios as presented here in individual droplet nuclei [Zhang and Anastasio, 2001]. Organic compounds may enter droplets through chemical reactions once a cloud is formed [Russell and Seinfeld, 1998]. Therefore, the possibility that the organics in our sample did not themselves act as CCN, but were present as

secondary species, should be explored. The electron microscope has a near-vacuum environment, so only non-volatile particles were analyzed. Inorganic nitrate, while more volatile to the extent that it cannot be examined in vacuum, was present only in very low amounts in the INDOEX region [Gabriel *et al.*, 2002]. Ammonium sulfate does not completely volatilize under the conditions used in TEM and SEM and is readily detectable. The other important inorganic CCN species observed in INDOEX samples, sea salt, is very stable. Bilde and Svenningsson [2004] have shown that small amounts of inorganic species can increase the activation behaviour of slightly soluble organics. However, the low-dose high resolution imaging of our sample showed that there are definitely organic particles present in which no inorganic crystalline phase components could be detected. An analysis of our detection capabilities determined that inorganic species, if present, would have to comprise less than 0.01% of the particle volume. For the particular particles analyzed by EELS, which were imaged at lower resolution, the upper limit was still only about 0.025% by volume. Because these values are an order of magnitude smaller than those used by Bilde and Svenningsson [2004] and cloud drops do not form in the atmosphere without a nucleus, we conclude that the pure organic particles measured in our sample acted as CCN.

3. Conclusions

[12] Our analysis indicates that organic species do not have to be mixed with inorganic particles to act as CCN, and that organo-nitrogen compounds nucleate cloud droplets in the Indian Ocean. If these particles are present in other polluted areas, they could contribute substantially to the global indirect aerosol effect.

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